

Chemical and Vibronic Shifts in the High-Resolution Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectra of Polystyrene Isotopomers

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INTRODUCTION

Vibronic features in NEXAFS spectroscopy are created when the excitation of a vibrational mode accompanies a core excitation transition (i.e. $C\ 1s(v=0) \rightarrow \pi^*(v=1)$). We have used the SGM monochromator at beamline 7.0.1. to acquire the high resolution $C\ 1s$ Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra of hydrogenated and deuterated polystyrene. These results present unambiguous evidence for a vibronic contribution to the fine structure in the $C\ 1s(C-H) \rightarrow 1\pi^*_{C-C}$ transition in polystyrene. These results enable us resolve the relative magnitude of the chemical and vibronic shifts in the shape of the characteristic $C\ 1s(C-H) \rightarrow \pi^*_{C-C}$ transition in polystyrene.

RESULTS AND DISCUSSION

Samples of hydrogenated and deuterated polystyrene (H-PS, D-PS) were obtained from Polymer Sciences. Thin films ($\sim 1000\ \text{\AA}$) prepared by spin casting were adjacently mounted on a TEM grid so that the spectrum of each material could be obtained simultaneously by “image sequence” acquisition methods[1] in the BL 7.0.1. Scanning Transmission X-ray Microscope (STXM). By recording the incident flux (I_0) and the transmitted flux for each polymer (I_{DPS} , I_{HPS}) by imaging at each energy in a conventional spectral scan, the effects of low frequency noise, mechanical drift and beam decay are reduced, and the potential for energy shifts between the spectra is eliminated. The resolving power of the monochromator was 6100 when these polymer spectra were acquired, as determined by fitting the Rydberg transitions in CO_2 gas to an approximate Voigt function.

Figure 1 presents the highly structured $C\ 1s \rightarrow \pi^*$ absorption band from the NEXAFS spectra of hydrogenated polystyrene (blue line) and deuterated polystyrene (red line with points). The difference between the spectra of hydrogenated and deuterated polystyrene provides *prima facie* evidence for vibronic effects, since the C-H vibrational stretch energies change systematically with the hydrogen isotope mass[2].

Similar vibronic effects were observed previously in benzene isotopomers by Ma *et al*[3]. Since a carbon atom is symmetry equivalent in the ground electronic state of benzene, no chemical shifts will be present in the $C\ 1s$ NEXAFS spectrum of benzene. In polystyrene, vibronic effects similar to those observed in benzene are convoluted with the chemical shifts from the symmetry inequivalent sites on the phenyl ring. High quality *ab initio* calculations are used to resolve the chemical shift contributions from vibronic effects. These effects are found to have a similar magnitude. A discussion of these calculations and spectroscopic simulations presented elsewhere[4].

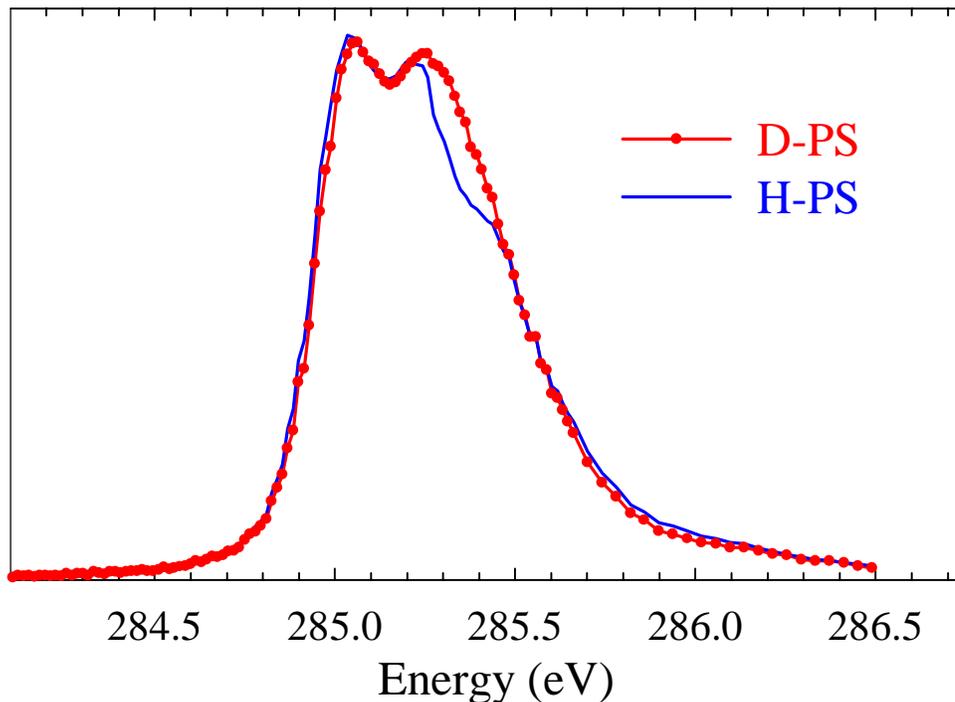


Figure 1. C 1s Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra of hydrogenated (blue line) and deuterated polystyrene (red line with points) recorded on the BL 7.0 beamline at ALS with a resolving power of about 6100. The area of the C 1s \rightarrow π^* transition has been normalized.

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